Phase behavior of a cell fluid model with Curie-Weiss interaction

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INTRODUCTION

In [1,2], we introduced a simple Curie-Weiss type model of a single-sort continuum particle system in which space $R^3$ is divided into congruent (cubic) cells. For a bounded region $V \subset R^3$ consisting of $N_v$ such cells, the attraction between each two particles in $V$ is set to be $g_v / N_v$, regardless of their positions. If such two particles lie in the same cell, they repel each other with intensity $g_r > g_v$. Unlike [3], we deal with the grand canonical ensemble. We proved (see [1,2]) the possibility of a strict transition from a continuous system of interacting particles to such a cell model and the exact calculation of its grand partition function. As a result, the existence of a cascade of first-order phase transitions in the cell model with the Curie-Weiss interaction is strictly mathematically proved. Now we refer to the exact calculation of the state of the model (see [1,2] for details) and focus on important additions to the existing results of analytical calculation and quantitative analysis of the phenomenon.

THE MODEL

The equation of state (EoS) is a good tool for studying the properties of any system, e.g. obtained from the ratio

$$ PV = k_B T \ln \Xi ,$$

where $P$ is the pressure of a system, $V$ is its total volume, $k_B$ is the Boltzmann constant, $T$ is the temperature, and $\Xi$ is the grand partition function (GPF). In the case of a continuous system of $N$ interacting particles, the GPF has the form [4]

$$ \Xi = \sum_{n=0}^{\infty} \frac{z^n}{n!} \int \prod x_i dx_i \exp \left[ -\frac{\beta}{2} \sum_{x,y} \Psi_\Delta(x,y) \right] ,$$

where $z = \exp(\beta \mu)$ is the activity, $\mu$ is the chemical potential, $\beta = (k_B T)^{-1}$ is the inverse temperature, $\eta = \{x_1, \ldots, x_N\}$, $x_i$ are the coordinates of the $i$-th particle. If the system volume conditionally divided into a finite number of congruent mutually disjoint cubic cells $\Delta_1 \cdots \Delta_n \in (-c/2, c/2)^3 \subset R^3$, each of volume $v = c^3 = V / N_v$, the potential energy is written as [2]

$$ \sum_{x,y \in \eta} \Psi_\Delta(x,y) = \sum_{I \subseteq \eta} U_{\gamma(\eta)}(n) \rho_\gamma(n) ,$$

here $\gamma(\eta) = \sum_{x \in \eta} \rho_\gamma(x)$ is the occupation number of an $I$-th cell Here $\rho_\gamma(x)$ is the indicator of $\Delta_\gamma$, that is, $\rho_\gamma(x) = 1$ if $x \in \Delta_\gamma$ and $\rho_\gamma(x) = 0$ otherwise.

THE POTENTIAL OF INTERACTION $U_{1,2}$

$$ U_{1,2}(x,y) = \begin{cases} -\frac{g_r}{\beta}, & x \in \Delta_1, y \in \Delta_2, I_1 \neq I_2; \\ g_r > g_v > 0 & [1] \text{the condition of stability.} \\ \end{cases} $$

Optimization of thermodynamic variables:

$$ p = \beta g_v, \quad f = g_r / g_v $$

Solution of the GPF

Asymptotic solution of the GPF in the case of Curie-Weiss interaction is

$$ \Xi = \exp(N_v E_0(\mu)), $$

$$ z = \Xi \text{ when } E_0(\mu) = \max E_0(\mu), $$

$$ E_0(\xi) = \ln K_0(\xi) - \frac{1}{2} \left( \frac{K_1(\xi)}{K_0(\xi)} \right)^2 . $$

$K_0(\xi)$ are the special functions

$$ K_0(\xi) = \sum_{n=0}^{\infty} \frac{n! n^m \exp(-f \mu / 2 v^2)}{n!} \exp(xn) $$

BEHAVIOR OF THE CHEMICAL POTENTIAL

$$ \frac{\partial E_0(\mu)}{\partial \mu} = 0, \quad \Rightarrow \quad \beta \mu = \xi - \frac{K_1(\xi)}{K_0(\xi)} $$

AVERAGE DENSITY

$$ \eta = \frac{(N)}{V} = \frac{n}{v} = 1 - \frac{\partial \ln \Xi}{\partial \mu}, \quad \Rightarrow \quad \frac{\partial \mu}{\partial \mu} - \frac{K_1(\xi)}{K_0(\xi)} $$

PARAMETERS OF THE CRITICAL POINT

Parameters of the inflection points for first three $(\mu)$ phase transitions in the cascade $(\varepsilon = 1, f = 1.2)$

1. Extrema points of the chemical potential

$$ \frac{\partial \mu}{\partial \varepsilon} = 0 $$

2. Global maxima points of the chemical potential

$$ E_0(z_1) - E_0(z_2) = 0, \quad \mu(z_1) - \mu(z_2) = 0 $$

EXTREMA AND GLOBAL MAXIMA

CONCLUSIONS

- An accurate calculation shows that a one-component cell model with Curie-Weiss potential has a sequence of first order phase transitions at temperatures below the critical one. Emergence of such a cascade is possibly associated with the point nature of particles. The appearance of phases with higher and higher density in such a model is due to the lack of a term in the potential of interaction that would prohibit the excess concentration of particles in the cell.
- We derived conditions and relations for the values of the critical point parameters. We analyzed the mechanism of phase transitions based on the behavior of the chemical potential as a function of density.
- The obtained phase diagram confirms the absence of a triple point in such a system.

REFERENCES